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**STOPPING
WATER POLLUTION
AT ITS SOURCE**



MISA

Municipal/Industrial Strategy for Abatement

Water Quality

KAMINISTIKUIA RIVER WATER QUALITY

STUDY PART 4:

IMPACT MODELLING

OF EFFLUENT DISCHARGES

JULY 1990



Ontario

Environment
Environnement

Jim Bradley, Minister

KAMINISTIQUIA RIVER WATER QUALITY
STUDY PART 4: IMPACT MODELLING
OF EFFLUENT DISCHARGES

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FOREWORD

The study of the Kaministiquia River, originally planned as a waste assimilation capacity investigation in 1985, was subsequently expanded and included as a Municipal Industrial Strategy for Abatement (MISA) pilot site. Inclusion of the MISA objectives for the site study expanded the range of investigation from traditional nutrient and oxygen consuming waste concerns to include all known and suspected contaminants from point source discharges to the river.

Part 1 of the Kaministiquia River water quality study presented the findings of water quality surveys carried out in 1986 as they relate to the assimilative capacity of the lower river. The findings focussed on the impact of oxygen consuming wastes. A traditional one-dimensional riverine model was utilized to define the dissolved oxygen depletion.

Part 2 of this series presented the findings on the thermal structure and hydrodynamics of the river based on a joint study between the Ontario Ministry of the Environment and Environment Canada.

Part 3 of this series presented the findings on oxygen depletion in the river based on further work of the joint study between the Ontario Ministry of the Environment and Environment Canada. The waste assimilation capacity of the lower river was evaluated utilizing two-dimensional estuary modelling techniques. The findings focused on the impact of oxygen consuming wastes, and the detailed spatial distribution of oxygen.

This report, which is Part 4 in this series, presents the findings on 2,4,6 Tri-chlorophenol, Chloroform and Aluminum based on further work of the joint study between Ontario Ministry of the Environment and Environment Canada. A general water quality model based on the previously developed oxygen model is used.

Application of the above models to other rivers will be presented in future reports.

In addition to the MISA study activities, the entire Thunder Bay near shore area is under investigation as part of the Remedial Action Plan (RAP) process.

ABSTRACT

A general water quality model was developed and tested for 2,4,6 Tri-chlorophenol/Suspended Sediment, Chloroform and Aluminum for the Kaministiquia River as part of the development of water quality models for the Municipal Industrial Strategy for Abatement (MISA) program. The model is capable of accepting kinetic formulations; as a result, simulation of almost any contaminant is possible. The model is based on the previously developed 3 layer 16 segment Dissolved Oxygen-Biochemical Oxygen Demand box model (McCrimmon et al., 1988). Transport is calculated using the previously modified DYRESM model (McCrimmon et al., 1987) and accounts for the intrusion of cooler Lake Superior water which creates thermal stratification.

Simulations were carried out for the period of August 11-15, 1986, and resulted in reasonably good results with root mean square (rms) errors of 24%, 160%, 29% and 14% for Suspended Sediments, 2,4,6 Tri-chlorophenol (TCP), Chloroform and Aluminum, respectively. The TCP rms error of 160% is high but the kinetics for TCP are difficult to measure in the laboratory. The lack of detailed TCP loading data also contributes to this high error.

INTRODUCTION

The lower Kaministiquia River located near Thunder Bay, Ontario, is subject to industrial pollutant loadings which often cause the river water quality, especially dissolved oxygen concentrations, to fall below desired levels (MOE, 1972, 1988). The Canadian Pacific Forest Products Company operates the largest pulp and paper mill in Ontario which discharges to the Kaministiquia River approximately 10 km upstream of Lake Superior (see Figure 1). Application of a riverine water quality model would normally be sufficient to determine viable solutions. However, the delta of the Kaministiquia River is unusual since cooler and cleaner Lake Superior water intrudes upstream along the river bottom, which creates a vertical thermal structure with a distinct thermocline similar to that observed in lakes. This phenomenon also results in both a horizontal and a vertical gradient of different contaminant concentrations since the polluted water is warmer and flows downstream nearer the surface. Therefore, a river water quality model that accounts for vertically varying concentrations is required.

In a previous study (McCrimmon et al., 1987), flow characteristics and water temperatures were determined for August 11-15, 1986, using a modified version of the one-dimensional dynamic reservoir simulation model, DYRESM. The river was divided into 16 connected segments which were simulated in turn using DYRESM in six-hour time steps. In a subsequent study (McCrimmon et al., 1988), a 3 layer

16 segment DO-BOD box model, which used the previously determined flows and water temperatures, was developed and calibrated for the 1986 data. In addition, data for June 15-21, 1987, was obtained and used to verify the DYRESM and DO-BOD models.

In this study, the DO-BOD model is modified and expanded into a general model. This general model allows for the interactive input of kinetic reaction formulations and other required inputs so that almost any contaminant can be simulated. The model is tested for the 1986 period for 1) 2,4,6 Tri-chlorophenol (TCP) reacting with Suspended Sediments (SS) using equilibrium and non-equilibrium conditions, 2) Chloroform and 3) Aluminum.

GOALS AND OBJECTIVES

The overall goal of the Kaministiquia River Water Quality Modelling Study is to develop and verify water quality models with predictive capability for the assessment of possible management strategies for the Municipal Industrial Strategy for Abatement (MISA) program on pollution control for rivers of the same type. The goals and objectives of the MISA program were laid out in a White Paper from MOE (MOE, 1986). The objective of this study is to develop a general water quality model capable of simulating almost any contaminant that incorporates not only the multi-score, heated effluent conditions but also the modulations on parameter concentrations by the intrusion of the relatively cleaner, cooler and denser lake water.

This report describes the general model and the results obtained from testing the model for 2,4,6 Tri-chlorophenol/Suspended Sediments, Chloroform and Aluminum.

GENERAL WATER QUALITY MODEL

The method for predicting parameter concentrations involves a number of sequential steps, the results of which are used in ensuing steps. As outlined in previous reports (McCrimmon et al., 1987, 1988) these steps involve predicting water temperatures and flow characteristics using DYRESM and then using these results in the 3 layer box model.

The general water quality model developed is basically a more flexible version of the previously developed DO-BOD model. The new model is still a 3 layer, 16 segment model and retains the transport and diffusion components of the DO-BOD model but now the kinetic reactions of effluent parameters as well as initial conditions, loadings and observations can be inputted interactively. This allows for the creation of new models for simulating almost any parameter.

One to four parameters can be simulated in the model through this number could be expanded if required. The differential equation for a parameter used in the model is:

$$\frac{\partial C_i}{\partial t} = -u \frac{\partial C_i}{\partial x} + K_d V \frac{\partial^2 C_i}{\partial z^2} + a_1 C_1 + a_2 C_2 + \dots + a_j C_j \quad (1)$$

flow diffusion kinetics

and for the middle layer add the following

$$+ K_{EX} V \frac{\partial^2 C_1}{\partial x^2} \quad (2)$$

horizontal diffusion

where

- V = box volume (m³)
- t = time (d)
- x = horizontal distance (m)
- z = depth (m)
- i = index of parameters 1 to j
- j = number of parameters
- u = horizontal velocity (m/d)
- C = parameter concentration (mass/volume)
- a_j = relates changes of parameter C_j to parameter C_i
- K₂ = reaeration constant (d⁻¹)
- K_{EX} = horizontal diffusion rate (m²/d)
- K_d = vertical diffusion constant (m²/d)

Through experimentation of different model equation solutions, a predictor-corrector method using a 1/2 hour time step was selected for the DO-BOD model and is also used in the general model. It should be noted that to conserve mass the flow rates from the DYRESM results are used explicitly. In more detail, the model equations are solved as follows:

for time step 1: explicit solution (solve for C_iⁿ⁺¹)

$$V \frac{C_i^{n+1} - C_i^n}{\Delta t} = \text{flow} + \text{diffusion} + a_1 C_1^n + \dots + a_j C_j^n \quad (3)$$

for remaining time steps: 1) predictor (solve for \tilde{C}_i^{n+1})

$$V \frac{\tilde{C}_i^{n+1} - C_i^{n-1}}{2\Delta t} = \text{flow} + \text{diffusion} + a_1 C_1^n + \dots + a_j C_j^n \quad (4)$$

2) corrector (solve for C_i^{n+1})

$$V \frac{C_i^{n+1} - C_i^n}{\Delta t} = \text{flow} + \text{diffusion} + \frac{a_1 C_1^n + a_1 \tilde{C}_1^{n+1}}{2} + \dots + \frac{(a_1 C_1^n + a_1 \tilde{C}_1^{n+1})}{2} \quad (5)$$

where Δt is the time step and n is the time step level. For each time step, the predictor calculation is performed for all boxes then the corrector is performed for all boxes to achieve the simulated value, C_i^{n+1} .

The $a_i C_i$ terms can be inputted interactively into the model in an explicit form for each parameter, C_i , of each layer. The model then automatically converts the explicit formulations into the predictor and corrector forms and creates the new model.

DATA BASE

Flow rates and water temperatures for August 11-15, 1986, were taken from previous studies (McCrimmon et al., 1987, 1988). Other data required for calibration of the model, such as loadings and

observations, were supplied by the Ontario Ministry of the Environment (MOE). In this section, the available data, calculated and estimated data and assumptions related to the data and model are presented.

The Kaministiquia River is located in northern Ontario near Thunder Bay. The stretch of river under investigation extends from the river outlet at Lake Superior to approximately 10 kilometres upstream, and includes the McKellar and Mission River branches, as depicted in Figure 1. The points A through P in Figure 1 indicate the cross-section locations at which parameter measurements were made by the MOE. By using these points and the added point Z, which is the location of the river's main pollutant source, as boundaries, 16 river sections were created for modelling purposes.

Model Data

The general model is tested for TCP/SS, Chloroform and Aluminum over the period of August 11-15, 1986. Flow, water temperature and hypsometric data were taken from the DYRESM calibration data base and results. The parameter observations supplied by MOE included 1) 8 hourly surface values for 2 days at 3 cross-sections for TCP, at 11 cross-sections for Chloroform and at 12 cross-sections for Aluminum, and for 4 days at 15 cross-sections for SS, 2) a few isolated observations of each parameter in the top and bottom layers at cross-sections G, I, M and P and 3) diffuser loading concentrations for each parameter on a 4 hourly basis for one day and on a daily basis for the

remainder of the period. The river segment values were then estimated as the average of the upstream and downstream cross-section values. The initial conditions were estimated using observations but the lack of lower layer observations led to the assumptions that the middle layer and the upper layer are initially the same and the lower layer, which is assumed to be cleaner due to the upstream flow of water from Lake Superior, was set to the low constant values of 1.0 ng/L for TCP, 1.0 mg/L for SS, 1.0 µg/L for Chloroform and 0.11 mg/L for Aluminum based on the minimum observed values of each parameter.

RESULTS

The development of the general water quality model for the lower Kaministiquia River involved: 1) the simulation of flows and water temperatures using a modified version of DYRESM, 2) the calculation of vertical diffusions for temperature using the 3 layer box model, 3) the simulation of sodium to check the transport processes of the 3 layer box model, 4) the application of the 3 layer box model for DO-BOD, and 5) the testing of the general model which is a modified and more flexible version of the DO-BOD model. In this section, the results of the general model tests will be presented. The other steps, 1-4, were reported earlier (McCrimmon et al., 1987, 1988).

2,4,6 Tri-Chlorophenol Simulation

The kinetic reactions used in creating the TCP model were based upon the assumption that only sorption, photolysis and possibly volatilization would be significant (National Research Council of Canada, 1982). Suspended sediment (SS) can absorb TCP and, therefore, is also simulated in the TCP model. Settling of SS is considered in the kinetic reactions. The total quantity of TCP is taken as the amount of TCP dissolved in the water plus the particulate amount, which is the amount of TCP attached to the suspended sediments.

Two TCP-SS models were created to test the assumption of particulate and dissolved TCP always being in equilibrium, which has been used for chlorinated benzenes (e.g., Stepien *et al.*, 1987). The first model, the equilibrium model, forces the particulate and dissolved TCP to be in constant equilibrium. The second model, the non-equilibrium model, does not force instant equilibrium but instead uses absorption and desorption rate constants. For the equilibrium model the fraction of dissolved and particulate TCP is calculated using a partition coefficient, PI, as

$$C_p/C_d = PI * C_{ss} \quad (6)$$

where C_p is the particulate TCP concentration (ng/L), C_d is the dissolved TCP concentration (ng/L), PI is the partition coefficient (L/mg) and C_{ss} is the suspended sediment concentration (mg/L). To calculate the concentrations C_p and C_d the equation

$$CT = C_p + C_d \quad (7)$$

can be combined with (6), where CT is the total TCP concentration. Volatization is not believed to have a significant effect upon TCP (NRCC, 1982) but is placed in the model for testing purposes. The undissociated form of TCP, which is expected to be the only form affected by volatization (NRCC, 1982), is calculated as

$$\% \text{ Dissociated} = 100 \frac{10^{-pK_a}}{10^{-pH} + 10^{-pK_a}} \quad (8)$$

where $pK_a = 5.99$ and the pH is approximately 7 in the Kaministiquia River. The resulting % undissociated is 8.9% so that the resulting model equations are

for TCP:

$$\frac{\partial VCT}{\partial t} = -u \frac{\partial VCT}{\partial x} + K_d V \frac{\partial^2 CT}{\partial z^2} - W A C_p - D V C_d - 0.089 V K_v C_d \quad (9)$$

flow diffusion kinetics

for SS:

$$\frac{\partial VC_{ss}}{\partial t} = -u \frac{\partial VC_{ss}}{\partial x} + K_d V \frac{\partial^2 C_{ss}}{\partial z^2} - W A C_{ss} \quad (10)$$

where W is the settling rate of SS (m/d), D is the decay rate (1/d) and K_v is the volatization rate (1/d). A volatization rate of 127.9

(cm/d) (NRCC, 1982) is applied to the surface layer, which has a mean depth of 75 cm. The resulting K_v used in (8) for the surface layer is 1.7053 (1/d).

Suspended sediment concentrations were calibrated first since they are independent of TCP. The main source of SS loading was the Canadian Pacific Forest Products Company diffuser at segment ZB. Measurements of loadings as well as observations at most cross-sections were taken approximately every 8 hours. It was found that reducing the SS settling rate to zero from the original rate of 2.0 m/d resulted in reasonably good simulations of SS with a root mean square error of 24%. An example of a typical surface layer SS simulation compared to observations is presented in Figure 2 for August 13, 1986. The observations are seen to be approximately equal at all points below the loading point at ZB, which indicates very little settling is occurring.

For the simulation of TCP a partition coefficient of 0.00053 L/mg, which was estimated from Fraser River Data, was used (J.H. Carey, pers. comm., 1988; Lam et al., 1988). This value of P_I is small and will result in TCP being mostly dissolved. The diffusion rates used were the same as those used in the DO-BOD model calibration of August 11-15, 1986. A decay value of 0.173 (1/s), which is equivalent to a 4 day half-life, resulted in an rms error of 160% for TCP. This rms error is large compared to the SS simulations but the relatively sparse input and observation data did not allow for a reasonable calibration. When the volatilization option was not used the

surface layer values of TCP increases 10%, on average, by the end of August 15, 1986. Also, the rms error increased to 180% suggesting that volatilization is a significant factor on the TCP concentrations of the surface layer.

A plot of the simulated and observed top layer TCP concentrations at the end of August 13 is presented in Figure 3. In Figure 3, the simulated values decrease downstream of the main diffuser at ZB due to photolysis and volatilization. In general, TCP diffuses into the ZB top layer segment from the lower layer and then is transported downstream.

The creation of the non-equilibrium TCP-SS model was similar to the equilibrium model except instant equilibrium is assumed to not occur so that an absorption rate, K_a , and a desorption rate, K_d , are used similar to Taylor (1987) as follows:

$$\text{if } C_d > C_{de} \text{ then } dC_p/dt = -dC_d/dt = -K_a (C_d - C_{de}) \quad (11)$$

$$\text{if } C_d < C_{de} \text{ then } dC_p/dt = -dC_d/dt = -K_d (C_d - C_{de}) \quad (12)$$

where C_{de} is the equilibrium value of C_d which is calculated using (6) and (7). Also, since C_p and C_d are not in equilibrium they were simulated separately as opposed to calculating them from (6), (7) and (9).

The results of the non-equilibrium model were very similar to those of the equilibrium model. This is due to the assumption that the diffuser loadings of TCP were in equilibrium which caused the concentrations in the river to be near equilibrium. Therefore,

equations (10) and (11) had little effect even when K_a and K_d were set to zero.

In general, the SS concentrations were well simulated, but the TCP concentrations were not simulated as well due to the lack of measured TCP loadings and observations. More data and a better understanding of 2,4,6 TCP kinetics are required to truly test the TCP-SS model.

Chloroform Simulation

Chloroform data for the August, 1986 period was used to further test the general model. The main assumption used for Chloroform was that decay is the only significant factor besides flow and diffusion. Reasonably good results were achieved under this assumption.

The governing differential equation for this model is

$$\frac{\partial VC_c}{\partial t} = \underbrace{-u \frac{\partial VC_c}{\partial x}}_{\text{flow}} + \underbrace{K_d V \frac{\partial^2 C_c}{\partial z^2}}_{\text{diffusion}} - \underbrace{D V C_c}_{\text{kinetics}} \quad (13)$$

where C_c is the concentration of Chloroform. Using a decay rate of 0.35, which is equivalent to a half-life of 2 days, resulted in rms error of 29%. Observations were only available for the surface layer so the rms error is only for the surface.

Time series of the surface layer Chloroform concentration (CLF) are plotted for segments BC and JK in Figures 4 and 5, respectively. On August 12 there is increased loading of chloroform which is evident by the peak in the time series plot at BC. After this time the concentration is seen to decrease due to lower loadings. Downstream, at segment JK, the peak is noticeably smaller, due mainly to decay, and occurs approximately 16 hours later. In general, the simulated values agree reasonably well with the observations.

Aluminum Simulation

The simulation of total aluminum was attempted using the general model. This was a relatively simple test since it was assumed that the aluminum was unreactive and there were no kinetic reactions.

The first simulations of total aluminum resulted in a low rms error of 14%. Both the plot of the surface layer at August 13, 2400 hours in Figure 6 and the time series plot of segment FG in Figure 7 show good agreement between the simulated and observed concentrations.

CONCLUSIONS

A general water quality 3 layer box model utilizing a predictor-corrector solution method and a 1/2 hour time step has been developed from the previously developed DO-BOD model (McCrimmon et al., 1988).

The general model is flexible in that it can simulate up to 4 parameters. Also, the kinetics of each parameter can be entered into the model so that a new model can be created for simulating almost any parameter desired. Therefore, the model still needs to be verified for organic pollutants.

In this study, the general model was used to create models for simulating 2,4,6 Tri-chlorophenol/Suspended Sediments, Chloroform and Total Aluminum. Reasonably good results were achieved for all parameters (rms errors less than 30%) except for TCP, which had a rms error of 160%. The higher errors for TCP are due, likely, to the fact that chlorophenols and the associated kinetics are not as well understood as the other parameters and that the TCP concentrations are difficult to measure. The input data for TCP are also poor.

Reasonable simulations of different parameters using the general model indicate the model is useful. However, most parameter observations were for the surface layer so it would be desirable to further test the model for parameters which have observations below the surface layer. As also outlined previously (McCrimmon et al., 1988), more detailed loading observations and possibly a better hydrodynamic model would likely improve the general models performance.

ACKNOWLEDGEMENT

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APPENDIX - FIGURES

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Figure 2. Simulated and Observed Top Layer Suspended Sediments

Figure 3. Simulated and Observed Top Layer Total TCP

Figure 4. Time Series of Top Layer Chloroform at Segment BC

Figure 5. Time Series of Top Layer Chloroform at Segment JK

Figure 6. Simulated and Observed Top Layer Aluminum

Figure 7. Time Series of Top Layer Aluminum

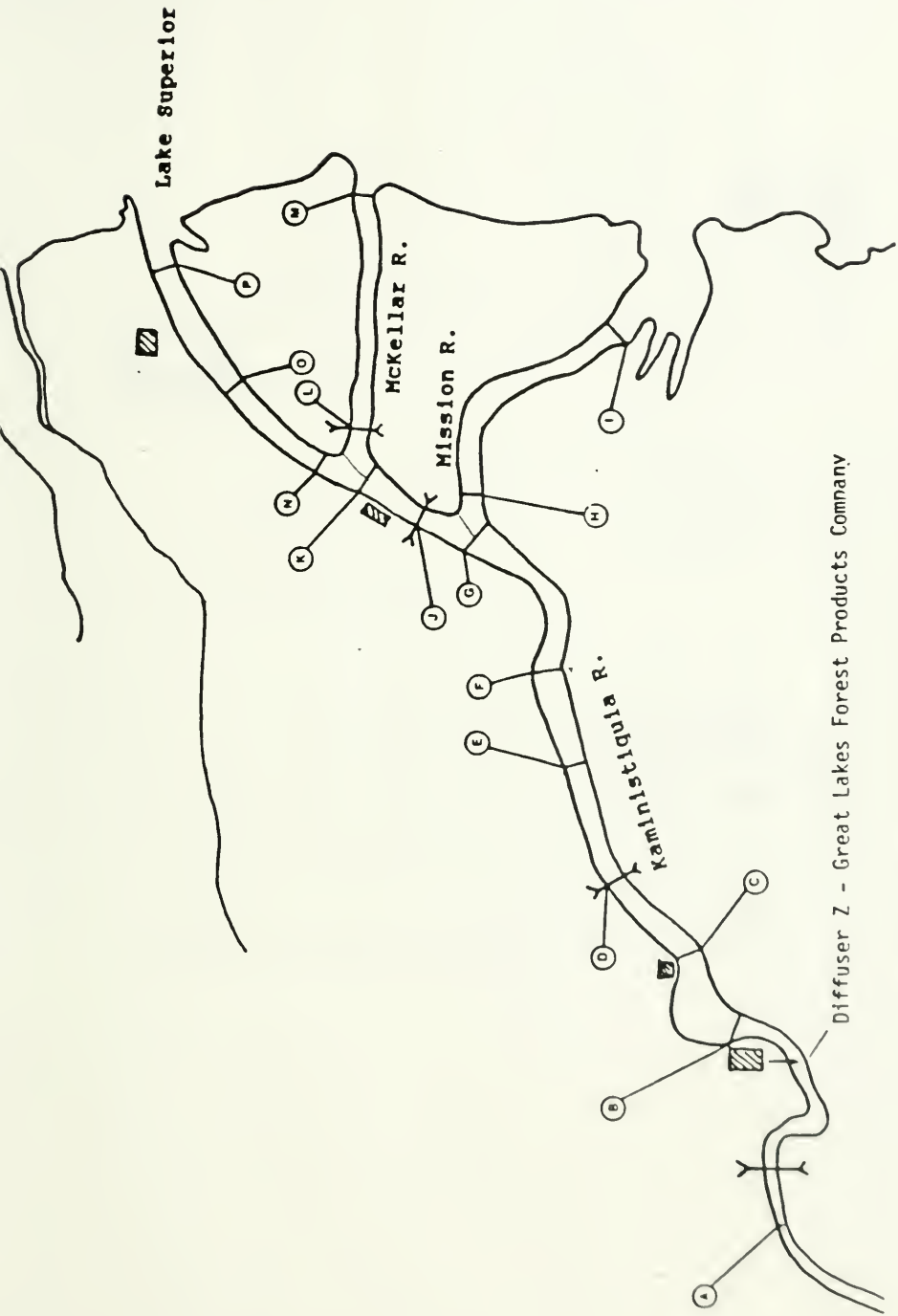


Figure 1. The Lower Kaministiquia River Study Area

Fig. 2

CSS MG/L
top layer
Aug. 13 1986
2400 hours

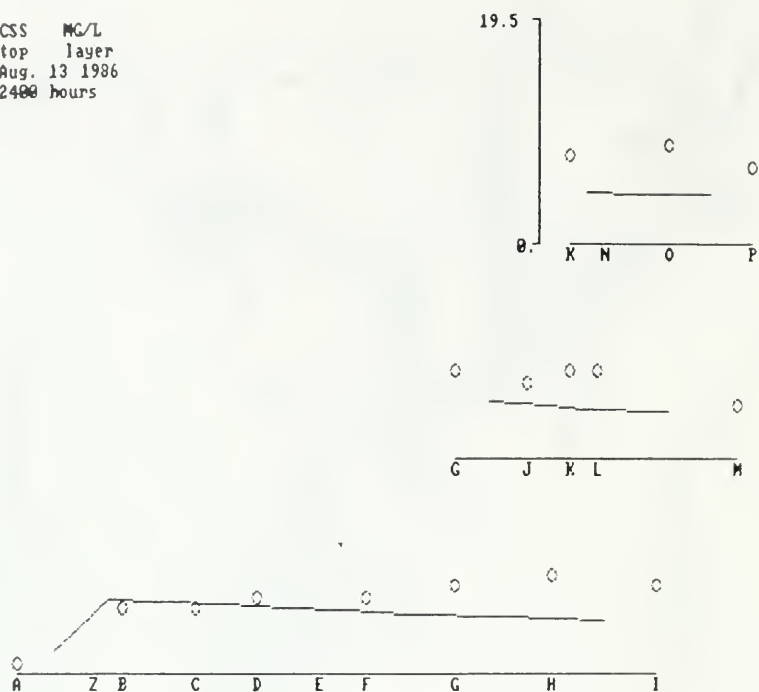
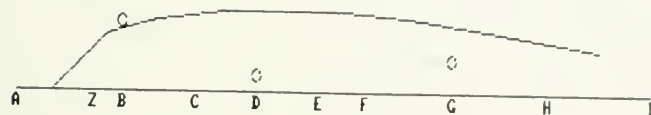
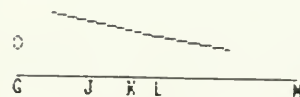
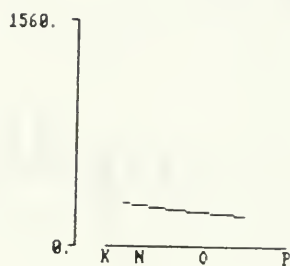


Fig. 3

CTO MG/L
 top layer
 Aug. 13 1986
 2400 hours
 99.7(%)Cd/Ct



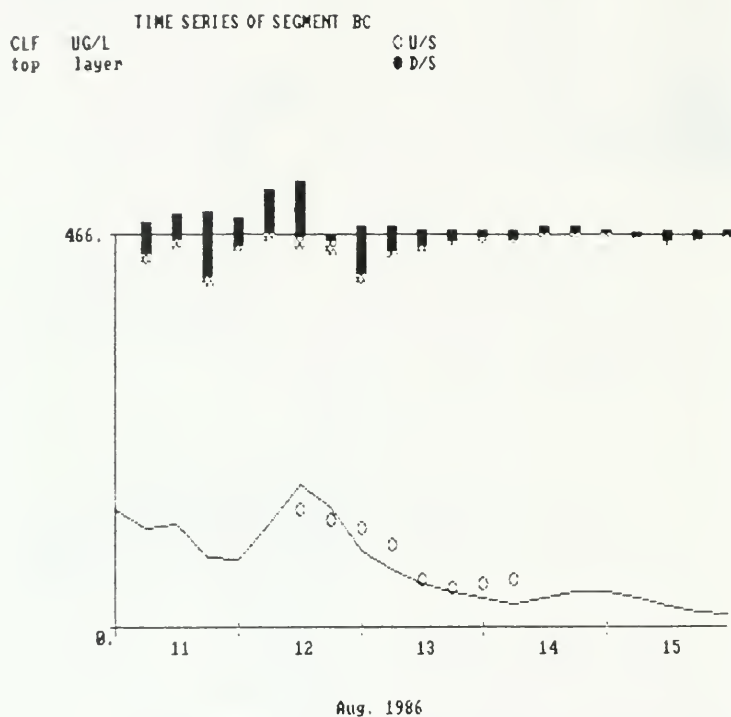
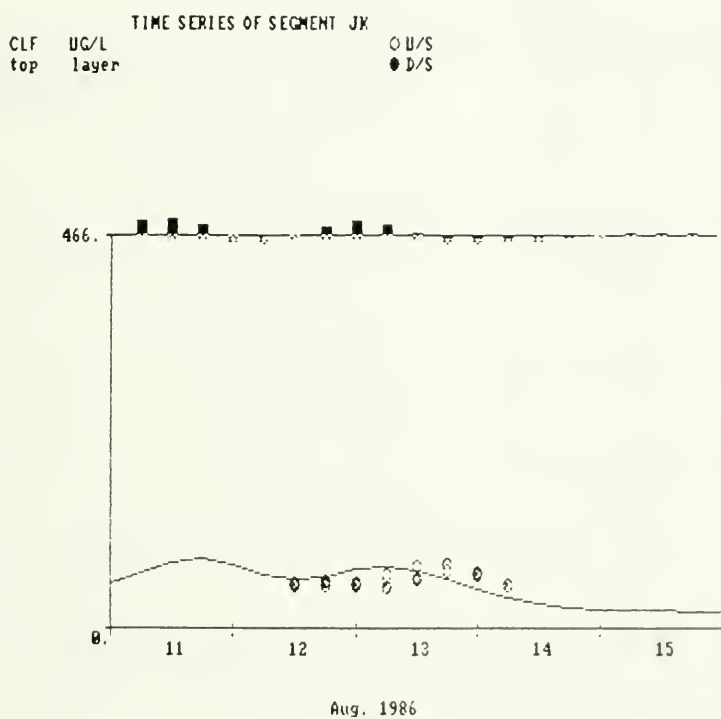


Fig. 5



TIME SERIES OF SEGMENT FG

ALL top layer

○ U/S
● D/S

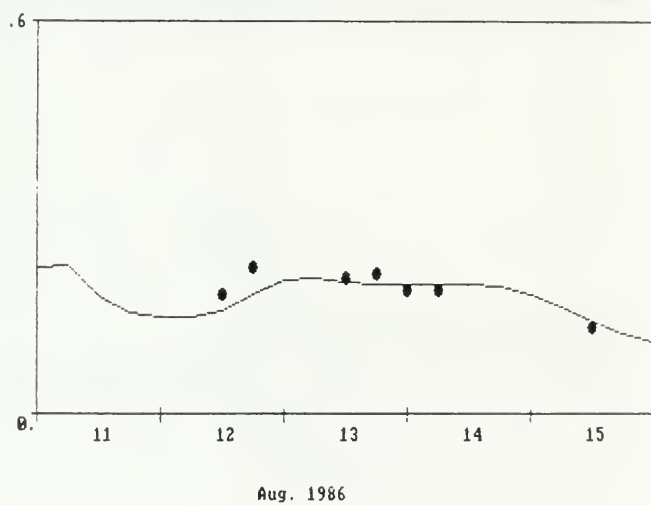


Fig. 7

ALW MG/L
 top layer
 Aug. 13 1986
 2400 hours

